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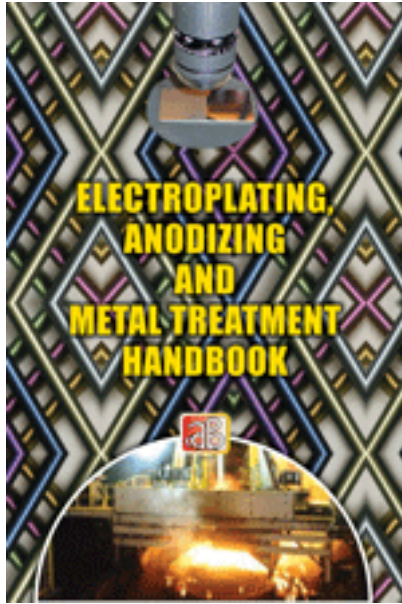
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Electroplating, Anodizing & Metal Treatment Hand

Book



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Surface finishing is a broad range of industrial processes that alter the surface of a manufactured item to achieve a certain property. Currently, the trend is towards surface treatments. Surface engineering techniques are generally used to develop a wide range of functional properties, including physical, chemical, electrical, electronic, magnetic, mechanical, wear-resistant and corrosion-resistant properties at the required substrate surfaces. In general, coatings are desirable, or even necessary, for a variety of reasons including economics, material conservation, unique properties, or the engineering and design flexibility which can be obtained by separating the surface properties from the bulk properties. Surface engineered products thus increase performance, reduce costs, control surface properties independently of the substrate and medium, thus offering an enormous potential in the finishing Industry. Electrodepositing of metals is a very significant industrial process. Electroplating is both an art and science. It entails adhering a thin metal coating to an object by immersing it into an electrically charged solvent containing the dissolved plating metal. Electroplating served a number of functions, such as protecting from corrosion and wear, decoration, and electrical shielding. Anodizing most closely resembles standard electroplating. Anodizing or anodizing is an electrolytic passivation process used to increase the thickness of the natural oxide layer on the surface of metal parts. Anodizing increases corrosion resistance and wears resistance, and provides better adhesion for paint primers and glues than bare metal. Anodic films are most commonly applied to protect aluminium alloys.

The aim of this handbook is to give the reader a perspective on several metal surface treatment techniques which are generally followed in the finishing Industry. This is a unique compilation and it draws together in a single source technical principles of surface science and surface treatments technologies of plastics, elastomers, and metals along with various formulae of bath solutions, current density, deposit thickness, manufacturing processes, various ingredients used in these processes. It is a very useful guide for the readers, engineers, scientists, practitioners of surface treatment, researchers, students, entrepreneurs and others involved in materials adhesion and processing.

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ELECTRO POLISHING

Electro polishing, an electrochemical process, is the reverse of electroplating. Therefore, metal is removed than deposited. The article to be electro polished is made the anode in an electrolyte which, when low voltage is applied, forms a polarized film over the entire surface. This film is thickest over the micro depressions. Where the polarized film is thinnest, electrical resistance is the least and therefore the rate of metallic dissolution is the greatest. Electro polishing selectively removes the microscopic high points much faster than the rate of attack on the "Valleys" or microdepressions. Stock is removed as a metallic salt. Stock removal is controllable and can be held to 0.0001 to 0.0025 in. However, stock removal can be much higher if desired, and under stringent condition can be held to a lesser amount. It is believed that the polarized film is responsible, under proper operating conditions, for brightening and smoothing the metal surface. It must be pointed out, however, that brightness and smoothness do not always go together. For instance, a welded or rough ground piece may be bright but not smooth. Conversely, a lapped surface may be smooth but not particularly bright.

When a metal surface is polished, the light rays are reflected in parallel lines, thus the surface acts like a mirror. On a rough or unpolished surface, the light rays are reflected in a random pattern; therefore, no image can be seen.

To obtain a smooth, highly reflective surface on various metals, several factors come into play. The degree of successful electro polishing is determined, to a large extent, on the surface conditions of the base metal. Poor conditions for electro polishing include nonmetallic inclusions, over pickling, heat scale, large grain size, directional roll marks, insufficient cold reduction or excessive cold working. Several of these conditions may be inherent in the metal as it comes from the mill. During electro polishing, metal is removed, revealing these flaws. When metal is removed smoothing can take place. Other factors contributing to a smooth, highly reflective surface are change in bath chemistry and precipitation of metal salts. When bath chemistry is out of balance, poor polishing or no polishing can result or an extended time may be necessary to obtain a satisfactory finish.

When salts build up in the bath, higher voltages are required to maintain the desired current density. This can result in burned contact points.

The Electro polished Surface

Comparison with Mechanically Finished Surface. The absence of scratches, strains, metal debris, and embedded abrasive characterizes the electro polished surface. It has the "true" crystal structure of the metal undistorted by the cold working that accompanies mechanical finishing methods.

The finishing by abrasives or other cutting or burnishing action, regardless of how small the amount of work, always distorts the surface. The important fact is the unavoidable presence of those rough ridges and loose clods of metal. Those defects are absent after electro polishing. The cold-work damages penetrates into the metal and the abrasive is embedded in the surface. It reveals in cross-section what are probably the rough ridges. The depth of damages is also revealed, which shows the surface without enough electro polishing to remove all the scratches and rough ride metal.

Much is known about heat-treating metals to relieve them of cold-work effects. The superficial damage done to a metal surface by mechanical finishing does not necessarily disappear as a result of heat treatments known to restore gross properties. Nor will heat treatment (or any other method) remove embedded and smeared-over abrasive particles.

Burnishing by lapping, buffing, or coloring decreases the micro inch roughness and improves the image-defining quality of a surface, but never completely removes the debris and damaged metal. The minimum of

cold work and mechanical damage is done in metallographic polishing, yet the effects are there. The fine abnormal structure of nickel plate reveals the presence of the cold-worked surface. The nickel plate clearly reveals the true, undisturbed metal in the electro polished surface.

The mechanical strength of the surface metal is lowered by cold work accompanying simple cutting operations. Machining of steel having 100,000 psi tensile strength can leave a surface skin of worked metal having only 35,000 psi tensile strength.

Advantage and Limitations

The preceding discussion shows some of the positive technical advantages of electro polishing. It shows why electro polishing produces a surface with good properties for: receiving electroplates having better smoothness, better appearance, and because of few voids, better corrosion protection; resisting corrosion when there is no plate or other coating; greater reflectivity of light and heat; better emissive in electronic tubes; and wear against other metal surfaces without loose metal fragments to cause fretting.

The surface damage and cold-work effects are overlooked if only smoothness is specified as a criterion of quality in a metal finish. As the preceding figure show, smoothness is not an independent variable in surface definition. It is only a part of an important subject that can be called "surface metallurgy." Smoothness specification, according to gages, can be met by electro polishing (with or without plating as an adjunct) just as well as by abrasive polishing.

The principal limitations of electro polishing are: the process cannot smear over and cover up defects such as seams and nonmetallic inclusions in metals; multiphase alloys in which one phase is relatively resistant to anodic dissolution are usually not amenable to electro polishing; heavy orange peel, mold-surface texture, and rough scratches are not removed by a practical amount of electro polishing and require "cutting down" first, just as needed before buffing and colouring. This last situation can be reversed, and electro polishing is used as a "roughing operation" before colour buffing on wheels.

Seams and nonmetallic inclusions impose a limitation. In showing up such conditions, electro polishing is a good inspection tool. Although unpassable by established inspection habits, an electro polished and plated. Table 7, 8 and 9 smoothness versus polishing, smoothness of steel and smoothness of brass and aluminium respectively.

Number shown is screen size of grit on the belt. Same locations as accurately as possible before and after mechanical and electro polishing. Average of several reading. All RMS units, where stated in this paper, are micro inches. Hand polishing. Automatic-machine polishing.

Electrobuff is a term used to designate the electro polishing of an electroplate as distinct from the electroplating of the basis metal. Both electro buffing and electro polishing remove metal. The nickel-plating operation adds metal. The group of plates was bright nickel; a mirror-like smooth electrodeposits. The group of plates was dull nickel, appearing smooth, but lacking luster. Surface can be superior in performance. Chromium plate has filled a hole left by electro polishing out a nonmetallic inclusion. The depression in the chromium plate at the site of the filled-in hole would be termed a "pit" and the part would be rejected. Yet, the inclusion would remain in an abrasively polished surface and be "bridged over" by the chromium plate. A point of weakness would exist, since the chromium would not adhere to the nonmetallic. The plated products would be passed by inspection.

Clearly, an informed approach to the use of electro polishing can give improved products, and processing costs can be reduced in many applications. By electro polishing, surface appearance and quality can be as easily reproduced as can an electroplate. Electro polishing baths are not so critical as plating baths to control and are less subject to contamination.

Types of Metal Electro polished

Most metal can be electro polished successfully but best results are obtained with those having fine grain

boundaries and free of nonmetallic inclusions and seams. Also, those comprising a high content of silicon, lead or sulfur are usually troublesome.

Stainless steels are the most frequently electro polished alloys and all can be electro polished. Castings will polish to a bright finish but not to the same brightness or smoothness as wrought alloys.

Besides stainless steel, other commercially electro polished metals include high and low carbon steel, copper, brass, beryllium copper, phosphor bronze and many grades of aluminium. Other metals, which can be electro polished, are columbium, gold, silver, tantalum, titanium, tungsten and vanadium.

Table 10 lists various metals and solutions, which are suitable for electro polishing.

There are numerous suppliers of proprietary solution on the market.

Today. Some are complete solutions while others are concentrates, which are mixed with acids purchased locally. Before purchasing a solution, each should be evaluated to obtain the best operating conditions for a particular application. Type of solution, operating temperature, ventilation requirements and pollution problems are some of the things to be considered.

Application

Stamping, spinning, weldments, castings, drawings, forgings and wire goods are all suitable candidates for electro polishing. Typical items fabricated from stainless steel and electro polished include hospitals, medical and surgical equipment; dairy, food and beverage processing and handling equipment; bone and joint implants; vacuum equipment; paper mill equipment; automotive and truck parts; electronic and communication parts; tubing, pipe, valves and fittings; fasteners and all types, sizes and shapes of wire goods. These parts can range in size from a small nut to tanks with thousands of gallons capacity.

Steel items are electro polished for micro inch improvement, burr removal and to obtain a better surface for electroplating. For instance, the I.D. of gun barrels are electro polished prior to hard chrome plating. electro polishing is used on brass costume jewelry items, electronic parts and as a finish prior to electroplating. electro polishing, by removing a small amount of metal from the surfaces, also removes any contamination on or just under the surface. This enables a much stronger subsequent weld or braze to be achieved, many times with less heat or brazing material being used.

Many times electro polishing has been used as an inspection tool. For example, during the fabrication of heavy walled stainless steel elbows, tees, crosses, etc. which are used in nuclear applications, it has been found that electro polishing was a superior method of crack detection than was the standard dye check. Cracks can develop in the surface which are not detectable by visual inspection and are ever suspect for x-ray inspection. electro polishing by removing the top surface, reveals material flaws such as cold shots, cracks and inclusions. This is not only valuable for nuclear applications but also for high-pressure systems. electro polishing is currently being used to decontaminate equipment used in nuclear power plants.

Reactor vessels, pipes, fittings, valves, heat exchange, tanks, etc. for the food chemical and pharmaceutical and polymer industries are currently being electro polished to provide a smooth, clean surface which provides greater anti-stick qualities coupled with easier cleanability. In many cases an electro polished stainless steel fabrication provided anti-stick qualities equal to glass lining. Other applications for electro polishing include decorative purposes and removing heat tint from spot welds, heli-arc welds and other types of welding. This is of great value for wire fabrications which have been spot welded.

Solution Operation

Over 90% of electro polishing is performed on stainless steel. All electro polishing is done in the same manner, therefore, our comments will be based primarily on stainless steel.

Various solutions are used for electro polishing, both acid and alkaline. The preponderance of solutions used commercially are acid and are based on one of the grades of phosphoric acid and one or more additional acids. Basically there are two types of electro polishing solutions- infinite and finite. When a part is being electro polished, a small amount of metal is removed. This metal in combination with components

of the bath form a metallic salt which drops to the bottom of the tank and forms a sludge. This bath has an infinite life. A finite solution is one in which metallic salts remain dissolved in the solution and do not settle to the bottom of the tank. To obtain optimum results these metallic salts must be held within limits. When the upper limit is reached, the solution must be decanted and replaced with new solution to keep the metallic salt concentration within satisfactory operating limits. This can be expensive because of the Resource Conservation and Recovery Act regulations for disposing of this used acid.

Infinite life solution requires that periodically the solution be removed from the tank and stored. The sludge in the bottom of the tank is then removed and disposed of according to RCRA regulations. The solutions.

The solution is then pumped back into the tank and fresh solution added to proper operating level.

In electro polishing, the parts are made the anode in the appropriate solution which will dissolve the oxides of the metal. As these metal ions are removed from the metal surface more metal atoms are exposed, thus polishing occurs. As in plating, a DC rectifier is used for the power source. As work is being electro polished oxygen is liberated at the anode and hydrogen is liberated at the cathode. Thus no hydrogen can be imparted to the part. There can be times when an imbalance of solution occurs and the oxygen liberated at the anode and present in air can cause an explosion of the hydrogen. Such explosions will be loud but not dangerous. This condition is preceded by a larger than normal foam blanket on the solution surface and is ignited by a spark from a work holder.

ALKALINE CLEANING

Although convenience of discussion requires that the subject of part preparation be separated into distinct areas, it is a mistake to think that these areas are not interrelated and interdependent. Rather than to think in terms of any single step, the plater is encouraged to think in terms of a preplating, or part preparation cycle, every step of which is terms affected by what went before, and in turn affects that which comes after.

The subject of this preplating cycle is to remove those surface films, which can be characterized as soils, and replace them with films, which will be compatible with the solutions being used to apply the final finish. When the sequence is properly selected and operated, the parts will enter the final processing solution with a surface in an activated or receptive state for the finish to be applied. To accomplish this preparation, four basic steps are required:

Gross cleaning- the removal of heavy soil.

Fine cleaning-the removal of residues from gross cleaning, along with fine particulate matter.

Oxide removal-the removal of the thin layer of oxide, which covers every metallic surface.

p^H adjustment-to bring the residual surface film close to the same p^H as the processing solution.

These basic steps constitute the objectives of each stage of the preplating cycle. The actual processing sequence may be considerably more elaborate. Any stage may require more than a single processing solution; some soils may require more that a previous stage be repeated; the rinsing steps must be considered as part of each stage, not merely incidental; if a multi-component plate is to be applied, intermediate activating or preparatory steps may be required. The complete process, therefore, can become extensive.

In addition to preplating cycles, there also may be less demanding cycles for other manufacturing operations; cleaning prior to applying rust preventives; cleaning prior to conversion coating; and specialized cleaning operations.

Factors which affect all of these processes include:

The nature of the soil

The base metal

The finish to be applied

SOILS

The definition of a soil may be compared to the definition of a weed. A weed is a plant that is out of place. A rose bush in a wheat field is a weed. A wheat stalk in a rose garden is a weed. Similarly, a soil is matter out of place. Rust proofing oil on a part in storage is not a soil. Only when the part moves to the finishing room does it become a soil. The same is true for cutting oils used in machining; drawing or stamping lubricants; buffing compounds, etc. The air is filled with particulate matter, oil sprays and various fumes, all of which can settle out on parts in storage and which are lumped together as shop dirt. A part cannot be made without contaminating it to some degree with some sort of soil.

Soils not only vary in their basic nature, but the same soil may present varied cleaning problems, depending on the method of application and its history. Some soils are particularly susceptible to these effects.

Buffing Compounds

Buffing compounds are mixtures of lubricating materials (usually fatty acids), abrasives (complex silicates, carbides or metal oxides) and materials to control the melting point (often high-melt paraffinic compounds or waxes). Since the buffing process is a friction related process, very high temperatures may be generated at the point of contact, and all the ingredients can react with each other and the metal surface. These temperatures can vary widely with buffing conditions; the reactions can vary as well. It is not unusual, therefore, to find that the same parts buffed with the same buffing compounds which then bind the residues to the surface, storage or transfer time between buffing and cleaning operations will also affect the cleaning process. In general, the shorter the delay between operations, the easier will be the cleaning process. In extreme cases of delay it is possible for the buffing residues to react so extensively with the surface, that when they are removed, an etch pattern will remain.

Rust-proofing Compounds

Rust-proofing compounds can roughly be placed in three categories:

1. Inorganic, water-soluble compounds for protection between operations, or short-term protected storage. These normally do not present any cleaning problems.
2. Emulsifiable organic mixtures cut back with water to form the required emulsion. When the emulsion "breaks" due to a change of temperature or the evaporation of water, the organic portion is left on the surface as a protective film. The formulation usually contains one or more volatile constituents, which evaporate with the water during drying so the protective film is no longer emulsifiable. Protection is adequate for long-term protected storage, or interplant transfer. Cleaning problems are similar to the next.
3. Solvent cutback organic mixtures provide a wide degree of protection, depending on composition and degree of cutback. Protection may be adequate to permit outdoor storage for reasonably extended periods. They may be formulated with water-displacing characteristics so parts to be protected may be immersed wet. The organic protective materials generally contain an oil base, a highly protective material such as a fatty acid, a metallic soap, or a polar material with an affinity for the substrate. If they are not fully dry to the touch they become magnets for shop dirt. Dryness or lack of tack is usually imparted by incorporating a wax, a drying oil or a film forming resin. Since these materials are designed to protect by preventing the penetration of moisture to the metal surface, they are often difficult to clean in aqueous systems. Solvent or vapour degreasing before aqueous cleaning is often helpful. A solvent dip to penetrate the film and reduce its viscosity also helps. If waxes are used for dryness, the temperature of the cleaning solution must be higher than the melting point of the wax.

Age of the film can be an important factor. Some of the polar materials may react with the metal surface. Unsaturated compounds may polymerize to form varnish-like materials. Evaporation of the solvent used for cutback will alter the viscosity. Coiled stock is particularly susceptible to these effects. Depending on the tightness of the coiling, these variations may occur at different rates in various areas of the coil. Hence, differences in cleaning requirements from point to point on the coil are not unusual.

Machining and Forming Oils

Increasingly often, these oils are being fortified with additives providing extreme pressure lubrication. Since these adhere strongly to the substrate, aggressive, high-alkalinity cleaners may be required. Machining and forming conditions by generating locally high temperatures can affect the cleaning process. Additionally, poorly designed or poorly maintained tooling can introduce surface conditions that complicate the cleaning process. Double-cleaning cycles may be required to compensate for these defects. Post-plating defects, including roughness, plate porosity, and spotting out can result from these causes.

Certain chlorinated or sulfonated oils may be gelled by high alkalinity cleaners, and low alkalinity materials may be more effective. Once gelled, they can be very difficult to remove. Where the presence of these materials is suspected, a sequence of low alkalinity followed by high alkalinity is the safest procedure.

Smuts

A smut is defined as finely divided particulate matter strongly adherent to the metal surface. It may be conductive or non-conductive. The non conductive smuts consist of inorganic residues including carbon from acid treatment of high-carbon steels, or from heat treating operations such as oil quenching or controlled atmosphere heat treatment; pigments from the use of pigmented drawing compounds; insoluble constituents of an alloy brought to the surface by previous chemical treatment; e.g., silicon in aluminum alloys, beryllium in beryllium copper, etc.; abrasive compounds from buffing or mass finishing operations; mold residues from casting operations; and certain types of shop dirt.

This type of smut usually responds well to reverse current treatment in electro cleaners or alkaline descalers.

The conductive smuts usually consist of metallic fines or finely divided metallic oxides from a previous operation such as polishing, mechanical finishing, machining or forming. This type of smut does not usually respond well to electrolytic treatment, since the gas is generated at the surface of the smut rather than at the metal surface. Much of the lifting action of the gas is therefore lost. Relatively strong or specialized acid treatment is often the only effective procedure. It is not uncommon for oil films to be trapped under these smuts so their removal results in the reappearance of a "water break". Double cleaning cycles may be required.

Both types of smut can occasionally be held to the surface by either electrostatic or magnetic attraction. Ultrasonic or spray cleaning may be required to overcome these forces.

Base Metal Effects

The nature of the base metal has a critical bearing on the type of cleaning system selected. Materials must be selected to provide the required cleaning action without undue or selective attack on the base metal. Since metals vary greatly in reactivity, allowable limits of pH, temperature and concentration and the type and concentration of inhibiting agents are dictated by the base metal. Cleaners for aluminum or zinc will generally be quite different from those of brass or steel.

Finish Effects

Some finishes are applied from solutions which either have cleaning and deoxidizing action by virtue of their composition, or which are very tolerant of marginal part preparation. Cyanide zinc plating solutions fall into this category, and it has been common practice to use very condensed, and often marginal preparatory cycles ahead of these solutions. The wisdom of the approach is highly questionable, but acceptable, if not high-quality, work can be produced in this way. Nickel-plating, on the other hand, is highly susceptible to improper part preparation, so more extensive and effective cycles must be used. Numerous other instances can be found to illustrate this point. Tests for Cleaning

The literature on various tests for the effectiveness of cleaning procedures is extensive. Unfortunately, with few exceptions, these remain research tools rather than production control methods. Among the methods suggested are analysis and control of numerous characteristics of the cleaning solution, the waterbreak

test, spray pattern test, atomizer test, residual soil measurements, residue pattern evolution, fluorescent dye evolution, radioactive tracer tests and the copper sulfate test.

In production, the cleaning process is usually controlled by a combination of solution analysis and the water break test.

Solution Analysis

The increasing complexity of cleaning blends, and the widespread use of proprietaries, has reduced control by solution analysis to simple test for solution concentration or total alkalinity, occasionally supplemented by an analysis for total surfactant concentration. These may be carried out by laboratory procedures, but most often are monitored with simple test kits provided by the suppliers. Dilute solutions, such as used in spray washing equipment, may be monitored by concentration measurements based on simple conductivity meters, or hand-held refractometers.

More extensive breakdowns involving measurements of p^H , complete titration curves, emulsification characteristics, surface tension, colloidal suspension properties, etc. are generally reserved for use by the suppliers laboratory in trouble shooting, cleaner selection or the development of new materials.

The Water break Test

This is based on the ability of a properly cleaned metal surface to retain an unbroken film of water. The test is subject to possible misinterpretation due to retained alkali from inadequate rinsing of cleaner residues, or the presence of hydrophilic smuts with oil trapped under the smut. These difficulties can be avoided by using a suitable acid treatment before making the observation. In production, parts are inspected at various stages of the preplating cycle for any evidence of "waterbreak" or failure to retain a continuous film of water.

The other tests listed for determining the cleanliness of a surface are used as research tools for evaluating cleaning mechanisms and developing new materials. Occasionally one or more of these techniques may be used as a control procedure in very demanding applications; e.g., sophisticated electronic manufacture, or space applications.

Cleaner operation

Emulsifiable Solvents

These are mixtures of suitable solvents and sufficient concentrations of surfactants to cause the solvent to emulsify when added to water. They may be used full strength followed by a water rinse; or as a prepared emulsion, generally at a concentration of 5 to 10% by volume in water. A residual film is always left on the metal surface. They therefore are generally used as precleaners. Cleaning is by dissolving action of the solvent on oily soils present on the surface, although the surfactants used to form the emulsion provide additional cleaning action. The prepared emulsions are frequently used in spray units. Increasingly stringent restrictions on the levels of hexane solubles in effluents are having a negative influence on the use of these materials since they contribute heavily to this type of effluent contamination.

Buffing Compound Removers

These are essentially highly specialized forms of soak cleaners, designed for the effective removal of buffing compound residues. They fall into three basic categories:

Neutral detergent-usually liquids; mixture of surfactants; p^H close to neutral with buffing provided by the surfactants used. Concentrations in the range of 1 to 10% by volume.

Enhanced detergent-similar to neutral detergent but fortified with organic alkalies which can react with the fatty acid in the buffing compound to form organic soaps. Concentrations 2 to 10% by volume.

Modified soak cleaners-similar to soak cleaners (q.v.) but modified to be especially effective on buffing compounds. Concentrations of 45 to 120 g/l (6 to 16 oz/gal).

Types 1 and 2 often show poor performance on oily soil other than buffing compounds. Temperature of operation should be above the melting point of the buffing compound, 60° to 80°C (140° to 180°F).

Use of ultrasound, or vigorous agitation will often permit operation at lower temperatures.

Alkaline Cleaners

Alkaline cleaners are blends of various inorganic alkaline salts with deflocculants, inhibitors and surfactants as required to provide the various cleaning mechanisms and functions discussed below.

Saponification

The chemical action by which a fatty acid, a fatty oil or other reactible soils is converted to a water-soluble compound such as a soap. Elevated temperature, concentration and p^H promote the speed and completion of the reaction. The main advantage is that cleaning will proceed in the absence of surfactants, and that the reaction products may function as additional cleaning agents to improve the performance of the cleaner.

Disadvantages include the fact that at least initially only reactible soils will be affected; the reaction products may build up to levels that cause rinsing and drying-on problems; incomplete rinsing may result in redeposition of the soils in a subsequent acid treatment; the solubilized soils unless separated will contribute heavily to hexane solubles in the effluent, and such separation is not always easy to attain.

Emulsification

The chemical process by which surfactants penetrate oily soils and break them down into globules sufficiently small to allow dispersion and suspension in the solution. Advantages include the fact that the reaction is often independent of p^H ; temperatures and concentrations required can be somewhat lower than with saponification; all types of oily soils will be removed; and rinsing will generally be somewhat better than for saponified soils. Disadvantages are similar to those for saponification except as noted, and with the added possibility that the surfactant concentration may be depleted at a rate different from the alkali depletion. The cleaner may therefore drift out of balance and fail to perform even when concentrations appear to be within limits.

Deflocculation

The process by which special chemical compounds surround particles of solid soil, removing them from the surface and dispersing them in solution. The process is generally improved by mechanical action and/or the development of gas by electrolysis. Elevated temperatures may also be helpful. Different deflocculants may be specific to certain solids, so complex soils may require mixtures of several agents for effective action.

Displacement

The process by which surfactants lift oily soils from the surface of the parts to be cleaned. A film of surfactant and solution is left on the part surface. The oily soil floats to the surface of the cleaning bath. Advantages include longer solution life and the possibility of operating at lower concentrations and temperatures. The main disadvantage is the need to continually skim the solution surface to remove the displaced oil. Failure to keep the solution surface properly cleared may result in the redeposition of the oily soil as the parts are removed from the solution. When properly operated, hexane solubles in the effluent are reduced, since the oily soil is constantly separated from the cleaning solution.

Spray Cleaners

Cleaning solutions, which are sprayed on the parts, sometimes under considerable pressure. Any of the mechanisms previously discussed, including emulsified solvents may be used. Careful attention must be given to choosing materials with low-foaming characteristics. The combination of chemical action and the mechanical action of the spray produces effective cleaning. Spray patterns must be designed to provide complete coverage of the parts, and the units given periodic maintenance to insure that nozzles are not plugged. Except for a foaming requirement, alkaline spray cleaners are similar to soak cleaners.

Concentrations and temperatures, however, are generally much lower, in the range of 15 to 30/g 1 (2 to 4 oz/gal) and 35° to 60°C (100° to 140°F). The newer low-temperature spray cleaners often operate at 4 to 15 g/1 (1/2 to 2 oz/gal) and 20° to 30°C (70° to 90°F). Liquid forms of the materials are sometimes available and operate at 1/2 to 2% by volume.

Ultrasonic Cleaning

The use in the cleaning process of ultrasonic energy provided by an ultrasonic generator which produces the necessary signal, and transducers which convert the signal to mechanical energy within the solution. The most commonly used frequency is probably 20 kHz, although higher frequencies (40 to 100 kHz,) are sometimes used. The ultrasonic energy alternately compresses and expands the solution and produces several concurrent effects.

Cavitation

The alternate pressure effects can literally tear the solution apart to produce "cavitation bubbles". When these "bubbles" are collapsed on the compression portion of the cycle, high-pressure mechanical effects are created, blasting solid soil away from the surface. Pressures as high as 180,000 psi may be generated. In extreme cases, the substrate being cleaned may be etched or otherwise damaged. Cavitation occurrence will be increased, and cavitation pressures reduced by increasing temperature. It disappears completely at the boiling point.

Electrical Effects

Very high voltage may be developed across opposite faces of the cavitation bubble. These can neutralize electrostatic charges holding particles to the substrate being cleaned, or even produce oxidizing effects by generating ozone from oxygen dissolved in the solution.

Transmission Effects

Since any relatively rigid material will transmit and re-reflect ultrasonic energy with only about 5% loss at each interface, ultrasonic cleaning is highly effective for blind holes, and internal threads or bores. Soft, resilient materials such as rubber and plastic are energy absorbers and therefore do not respond well to ultrasonic cleaning.

Cleaning Materials

Any of the standard cleaning material may be used with proper adjustment for the ultrasonic effect. Since much of the ultrasonic energy is converted to heat, solvents with low flash points or low boiling points may require cooling to avoid the possibility of fire or excessive evaporation. Alkaline cleaners will generally require better inhibition for sensitive metals, since the ultrasonic effects will increase the chemical action of the cleaner on the substrate. Cleaners can be specially formulated for ultrasonic use and /or to control cavitation pressures.

Equipment Considerations

The energy levels are generally calculated in terms of watt density/in.² of surface to be cleaned. Common values are 5 to 10 W/in.² since at higher levels a layer of heavy cavitation may form immediately adjacent to the transducer and prevent proper transfer of the energy into the solution. Only one side of the rack or part is used to calculate this "cleaning window". Transducer area must be adequate to provide the necessary energy without exceeding the 10 W/in.² limit mentioned above. Provision should be made to remove solid materials from the active area by filtration, or by settling, or avoid attenuation of the ultrasonic energy, or marking of the substrate by ultrasonically agitated abrasive particles.

Soak Cleaners

The work-horses of the industry, they remove the major portion of the heavy oily soils, and often some of the solid soils. They are generally used at 60 to 120g/l (8 to 16 oz/gal) with an average level of 75 to 90 g/l (10 to 12 oz/gal). Temperatures range from 50° to 95°C (120° to 200°F); more commonly 60° to 70°C (140° to 160°F). The newer, low-concentration, low-temperature materials will operate at 15 to 30 g/l (2 to 4 oz/gal) with a maximum of 45 g/l (6 oz/gal) at temperatures of 20° to 40°C (70° to 100°F) in the displacement mode and 30 to 60 g/l (4 to 8 oz/gal) with a maximum of 75 g/l (10 oz/gal) at temperatures of 25° to 40°C (80° to 110°F) in the emulsification mode. Soak cleaners consists of blended alkalies

to establish the desired pH range and reserve alkalinity, surfactants for detergency, and often deflocculants for the removal of solid soil. Inhibitors for specific base metals may be included. The pH range is usually established by the reactivity of the metal to be cleaned; strongly alkaline materials often being used for steel; magnesium and copper alloys, and mild materials for zinc, aluminum, brass and other sensitive alloys. Generally only relatively mild materials can be considered for all-purpose use.

Soak Cleaning Equipment

Plain steel equipment is usually satisfactory. Tanks should be equipped with a bottom drain, a dam type overflow for skimming action, a grease trap and a circulating pump if displacement type cleaners are used, and a heating coil.

Electro cleaners

Alkaline blends for use with current. Work can be either cathodic or anodic, although general practice now emphasizes anodic use. Cathodic electro cleaning has the advantage that twice as much gas is developed to provide scrubbing action to remove solid soils. Since the gas developed is hydrogen, sensitive metals may be subject to hydrogen embrittlement. Additionally, permissible levels of chromate contamination are considerably lower with cathodic cleaning, and metallic contaminants may be plated out onto the work. Good practice, therefore, dictates that when cathodic cleaning is used, special precautions are taken. These include use of sufficient anodic cleaning to remove plated on contaminants; prevention of hexavalent chromium contamination; and special care in regard to hydrogen embrittlement possibilities.

Electro cleaners are commonly used at concentrations of 60 to 120 g/l (8 to 16 oz/gal) with an average of 75 to 90 g/l (10 to 12 oz/gal); temperatures from 50 to 95 C (120 to 200F), more often 60 to 70 C (140 to 160F) and current densities of 5 to 15 A/dm² (50 to 150 ASF). The voltage required to develop the desired current density is dependent on the type of electro cleaner used, the tank configuration and the temperature. The normal voltage range is 6 to 12 volts. The newer, low-concentration, low-temperature materials will operate at 45 to 75 g/l (1 to 10 oz/gal) with a maximum of 90 g/l (12 oz/gal); temperatures of 45 to 75c (80 to 110F); current densities of 3 to 8 A/don² (30 to 80ASF). F07 sim8ilar equipment configurations, required voltage will be somewhat higher than for heated materials.

Electro cleaners consist of blended alkalis to establish the desired pH range and reserve alkalinity (generally at least some free caustic or other highly conductive salt is present to promote conductivity); inhibitors to prevent attack of the base metal (frequently silicates of one type or another); deflocculants and/or complexes for solid soil and must removal. Since precleaning has usually been carried out, surfactants are frequently limited to the amount needed to provide a mist suppressing foam blanket. Compromise materials with sufficient surfactant to act as both soak and electro cleaner are available. Foam levels must be watched carefully. The hydrogen and oxygen resulting from electrolysis will be trapped in the foam, and if foam levels are excessive, any sparks from poor contacts, vibration of racks, etc. can produce ear-shattering, although seldom dangerous, explosions.

METALS

In plating, as in many other manufacturing processes, "the chain is no stronger than the weakest link". While the plating may usually be considered the most complicated stage in an electroplating sequence, it may frequently be surpassed in importance by the "simple" step of rinsing.

Although many processing cycles are presented in this chapter, seldom will a given cycle meet the requirements of a particular case. Therefore, it is hoped that from the cycles given and the accompanying discussion, the reader will gain a sufficient understanding of the requirements in order to be able to plan the electroplating sequence which will be most suitable for each particular situation. It is of utmost importance for the reader to refer to other chapters to understand fully the various steps in a sequence. In addition, the cited references will be of great aid.

The most elementary cycle prior to the electroplating step is a simple sequence of cleaning and rinsing. In

the majority of cases, one or more additional steps, such as acid dipping, striking, activating, conditioning, etc., are required. Even in the above elementary sequence the cleaning may involve several steps. In order to understand and be able to project an electroplating sequence, the following fundamental factors and questions should be considered:

The work should be free of foreign matter such as oil, grease, dirt, and oxide before attempting to electroplate. Long transfer times allowing contamination and oxidation should be avoided.

Rinsing should be adequate. In many cases, it may be necessary to use distilled, deionized or A.S.M. type reagent grade water.

Acid dips, cleaning solutions and water should be of a composition so as not to leave films, which cannot be rinsed off. This means that the composition of the acid dip and cleaning solution will usually depend on the composition of the basis metal.

Does the basis metal require a special conditioning treatment prior to plating? Examples are the activation of stainless steel, immersion or anodic treatment for aluminum, and silver striking before silver electroplating.

In the solution formulas given in this chapter, the concentrations are

Expressed in metric units followed by English units in parenthesis, unless otherwise stated.

Liquids

Percent by volumes, %, as for example, 5% is equivalent to 5 liters in a total of 100 liters; grams per liter, g/L; (avoirdupois ounces per gallon, oz/gal; or fluid ounces per gallon, fl oz/gal).

Grams per liter, g/L; (avoirdupois ounces per gallon, oz/gal).

Unless otherwise stated, the acids used in the solution formulas are common technical or commercial grade concentrated acids that have the following approximated compositions:

Sulfuric Acid

Commercial 66 Beâ€™™ (93% by weight H₂SO₄). Sometimes expressed as g/L (oz/gal) of the 66 Beâ€™™ acid.

Hydrochloric Acid

(Muriatic Acid): Commercial 20 Beâ€™™ (31% by weight HCl)

Nitric Acid

Commercial 42 Beâ€™™ (67% by weight HNO₃).

Phosphoric Acid, Orthophosphoric acid: (75% by weight H₃PO₄).

Fluoboric Acid

(42% by weight HBF₄).

Acetic Acid- As Glacial: (99.5% by weight CH₃COOH).

Hydrofluoric Acid

(48% by weight HF).

Many of the chemicals referred to in this chapter are of a potentially hazardous nature. Before attempting to use them, the safe and proper methods for storing, handling, and disposing them should be thoroughly investigated.

Pretreatments

Pretreatment is the preparation of the article for the actual electroplating step. For clarity in discussion, pretreatment is divided into two stages- preliminary and final. The preliminary treatment removes heavy surface soils, such as grease, buffing compounds, drawing compound, scale, heavy rust and burnt oil.

Although it can be a part of the plating-room cycle, it frequently precedes it.

The final treatment removes only the last traces of oil and grease, and conditions the surface for electroplating. Acid dips in this final stage should not be expected to remove scale or heavy rust. They are only to neutralize the last traces of alkaline cleaner remaining after rinsing, and to activate the surface for electroplating.

In any preparatory cycle where the parts have both oil and oxide contamination, it is better practice to remove the oily material before attempting to remove rust or scale unless the oxide scale is to be removed by mechanical means. This will facilitate uniform removal of the latter.

Preliminary Treatment

This involves one or both of two basic steps: (1) Removal of heavy amounts of oil, grease, buffing compound, drawing compound, etc., and (2) removal of scale, heavy rust, burnt-in oil, etc.

These steps are only followed when required, as determined by the kind and degree of contamination. The methods for accomplishing step (1) may in most cases be used for all basis metals. The methods for accomplishing step (2) vary depending on the metal and type of article.

Removal of Grease, etc.

This may be accomplished by one or more of the following methods:

Spray cleaning. Alkali or emulsion-type cleaners are used with a nozzle pressure of 0.2 to 0.4 Mpa (30 to 60 psi.) The temperature, alkalinity, and time should be adjusted to suit the material being cleaned.

Solvent degreasing. Trichloroethylene or perchloroethylene is ordinarily used. The parts may be washed by agitation in a heated or cold liquid, or by vapour degreasing by suspending the cooled article in the vapour. Since the latter often leaves solid matter on the article, a multiphase operation is frequently used. This involves washing in a heated liquid, followed by dipping in a cool condensed liquid, and finally vapour degreasing. Proper health precautions should be taken, and because of fire hazard, the use of mineral spirits is not recommended. Solvent degreasing is usually followed by very thorough washing or preferably soak cleaning.

Soak cleaning. This is done by immersion, preferably with agitation, in alkali or emulsion cleaners and the same precautions should be taken as with spray cleaning.

Electrolytic alkali cleaning. This may be cathodic or anodic depending on the metal being cleaned and other conditions. Generally, the same conditions for a given metal are used as are given in the final cleaning cycle.

Cleaning of parts in bulk. Parts in bulk may be cleaned.

(a) Spray cleaning or solvent degreasing, holding the parts in suitable baskets or trays.

(b) Electrolytic cleaning in a high-conductivity cleaner using an insulated barrel cylinder will effect more complete removal of grease, etc., but may not be a necessary step in the preliminary cleaning cycle.

(c) The parts may be tumble-cleaned without current in a suitable cleaner.

Ultrasonic Cleaning

Used in conjunction with cleaning solutions to produce or increase agitation, which in turn facilitates the cleaning process.

Through rinsing should follow aqueous cleaning. Where there is a time lapse or storage period after cleaning, an alkaline cleaner film should remain on the part.

Removal of Scale, etc

Scale may be removed by the following methods:

Mechanical Treatment

This consists of polishing, tumbling, and sand, grit, or vapour blasting. Frequently this precedes or makes unnecessary any cleaning in the preliminary treatment cycle. If not complete, the mechanical treatment at

least reduces the alkaline treatment or acid pickling to a minimum. Where the scale is both heavy and tenacious, as with hot-formed, high-carbon steel parts, the practice is first to remove most of the scale by pickling. The polishing then removes the remainder of the scale and smooths the surface, which has been pitted and roughened by the pickling operation. On softer metals such as lead alloys, zinc and aluminum castings, and brasses, the thin surface oxide can be removed by fine mesh abrasive polishing or buffing, followed by cleaning the surface by passing it over a clean, dry buffing wheel.

Alkaline treatment

Alkaline descaling may be conducted on ferrous metal parts. A typical bath, which may be used as a soak or with current contains:

Sodium hydroxide	180 g/L (24 oz/gal)
Sodium cyanide	120 g/L (16 oz/gal)
Chelating agents	80 g/L (10.5 oz/gal)
Temperature	40 C (104F)

This method minimizes the effect of acid attack on the ferrous metal and will not produce smut, both of which could be a problem with acid pickling.

For removal of heavy scale, periodic reverse current (note 1) may be utilized.

Note 1- During periodic reverse (PR), the part is made alternately cathodic and anodic at intervals of a few seconds using DC current. Barrels or racks may be used:

Pickling

1. hydrochloric acid	20-85%
Temperature	Room
2. Sulfuric acid	5-15%
Inhibitor	consult supplier
Temperature	5-80 C (120-150F)
3. sulfuric acid	4-6%
Temperature	50-65 C (120-150F)
Parts as anode at	3.2-6.5 A/dm ² (30-60 ASF)
4. Hydrochloric acid	20-85%
Nitric acid	1-5%
Temperature	Room
5. Sulfuric acid	22.5 g/L (3 oz/gal)
Potassium nitrate	22.5 g/L (3 oz/gal)
Temperature	70C (160 F)
6. Sulfuric acid	45 g/L (6 oz/gal)
Ferrisul	37.5 g/L (5 oz/gal)

Note 2- Proprietary acids salts, many which contain fluorides, may be used along with or in place of the acid pickles.

Low-carbon steel. Solution (1) is used where the rust or scale is not heavy or tenacious scale. Solutions (2) and (3) are used for heavy and tenacious scale. Solutions (4), (5), and (6) may be used for brown, glazed or burnt-in oil surfaces/

High-carbon, casehardened, and low-alloy steels. High-carbon steel is usually hot-formed, producing heavy scale; low-alloy steels are cold-formed, producing little scale. These steels are susceptible to hydrogen embrittlement, and any pickling, except anodic, should be eliminated where possible or held to a minimum,

especially for spring-temper parts.

Cast irons. As with high-carbon steel, acid pickling of cast irons should be kept to a minimum since cast irons are susceptible to a low-hydrogen over voltage surface condition that causes low electroplating efficiency, and acid treatment will frequently intensify this effect. Formation of smudge can also result from over-pickling; therefore, scale, rust, and sand should be removed wherever possible by mechanical means.

If it is necessary to acid pickle, two solutions have been recommended:

1. Sulfuric acid	125 ml (16 fl oz)
Hydrofluoric acid	125 ml (16 fl oz)
Water	1 L (1gal)
Temperature	Room or elevated
2. Sulfuric acid	90 g/L (12 oz/gal)
Nitric acid	37.5 g/L (5 oz/gal)
Zinc	7.5 g/L (1 oz/gal)

Stainless steels. As with some other types of steel. Mechanical methods such as blasting shot penning, tumbling, and wheel abrading will prove economical prior to pickling. Iron-containing abrasive should not be used. Frequently, pickling of stainless steels consists of two steps: scale softening and final scale removal.

Scale Softening

Sulfuric acid	8-11%
Temperature	65-70 C (150-160F)
Time	10-45 min
Hydrochloric acid	10-15%
Temperature	50-60 C (120-140F)
Time	30-90 min

Inhibitors should be used and the parts rinsed thoroughly before going into the scale removal solution.

Scale Removal

Nitric acid	6-10%
Hydrofluoric acid	1.5%
Temperature	Room
Nitric acid	9-10%
Hydrofluoric acid	1.5%
Temperature	60-70 C (140-160F)

Solution (2) is used only for the austenitic stainless steels (except for type 303) to shorten the time required. The high-carbon grades (types 420, 440A, 440B, and 440C) should be mechanically descaled, if possible. Pickling in the fully hardened condition should be avoided to prevent pickling cracks. Other solutions for scale removal have been used:

Nitric acid	10%
Hydrofluoric acid	2.4%
Hydrochloric acid	1.2%
Temperature	55-60 C (130-140F)
Hydrochloric acid	25%
Nitric acid	5%

Temperature	50-70 C (120-160F)
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e. Copper and copper-base alloys. In addition to copper, the following solutions may be used for brasses, bronzes, and nickel silver, if buffed, descaling is seldom necessary.

Sulfuric acid	10-40%
Temperature	Room to 80° C (176F)
Sulfuric acid	60-70%
Temperature	50° C (120F)
Sulfuric acid	0-30%
Nitric acid	10-60%
Temperature	Room
4. Sulfuric acid	60-70%
Nitric acid	20-35%
Water	5-10%
Hydrochloric acid	0.1%
Temperature	Room
5. Nitric acid	25%
Phosphoric acid	75%
Temperature	Room

Solutions (2) and (5) and the so-called fire-off dip (3) can be used for removing heavy oxide, solution (3) sometimes being used after (1). For beryllium-copper, solution (2) is used. The bright dip solution (4) may be part of the preliminary or final pretreatment cycle, and it should be followed by very thorough rinsing. Solution (5) may be used for lighter oxides, but the parts should be clean and dry when immersed.

Final Treatment

It is assumed that the work going into the final cycle will be reasonably free of heavy contamination. As previously discussed, however, there is not clear demarcation between the preliminary and final treatments. Therefore, some of the cycles which follow will essentially be duplications of each other, the differences only being to allow for different degrees of cleaning necessary.

(I) Low-Carbon Steel

Cycle I-1

Anodic clean

Rinse

Acid dip (Note 3)

Rinse

Plate

Cycle I-2

Preliminary treatment

Rinse

Anodic clean

Rinse

Acid dip (Note 3)

Rinse

Plate

Cycle I-3

Anodic clean

Rinse

Acid dip (Note 3)

Rinse

Anodic clean

Rinse

Acid dip (Note 3)

Rinse

Plate

Cycle I-4

Preliminary pretreatment

Rinse, tumble in cleaner, no current

Warm rinse

Cold rinse

Acid dip (Note 3)

Rinse

Rinse

Plate

Cycle I-5

Anodic clean

Rinse

Acid dip (Note 3)

Rinse

Cyanide copper strike

Rinse

Acid dip " 5% sulfuric acid

Rinse

Plate

Note 3 " The acid dip may depend on the plating solution but is usually 4 to 10% sulfuric acid or 5 to 25% hydrochloric acid. Alkaline derusters are sometimes used in place of the acid dips. They are usually operated at 40 C (104F) and 2 to 5 A/dm² (20 to 50 ASF), with and without periodic reverse current (see Note 2). They would be followed by a rinse, acid dip, and rinse.

For nickel electroplating

Cycle I-1 through 1-5 may be used.

For copper (see also cycles II-8, II-9), zinc cadmium, and tin electroplating. The above cycles may be used, but very frequently a room temperature, 30 to 75 g/L (4 to 10 oz/gal) sodium cyanide dip or alkali dip for alkaline tin in used just prior to plating in the cyanide or alkaline solution.

For silver electroplating. Proceed after the last rinse in the above cycles as follows:

Cycle I-6

First silver strike

Second silver strike (Note 4)

Silver

Cycle I-7

Copper strike

Rinse

Silver strike (Note 4)

Silver plate

Cycle I-8

Nickel strike or plate

Rinse

Silver strike

Silver plate

Note 4- A rinse may be desirable after the silver strike. Its use will prevent a carry-over of impurities into the silver plating solution but will result in some loss of silver and cyanide.

For electroplating directly over steel, two silver strikes are necessary, as in cycle I-6. Cycle I-8 is usually preferred over I-7.

For gold electroplating proceed after the last rinse in Cycles I-1 through I-4 as follows:

Cycle I-9

Bright nickel strike

Rinse

Rinse

Active 37.5 g/L (5 oz/gal) KCN, Cathodic at 4.0 A/dm² (40 ASF)

Rinse in distilled or pure water

Gold plate

Cycle I-10

Copper, brass, silver, or nickel strike

Warm rinse

Rinse (distilled or pure water)

Gold plate (frequently a potassium cyanide dip and another rinse are used prior to gold plating in the above cycle)

For lead electroplating. Proceed after the last rinse in cycles I-1 through I-4 as follows:

Cycle I-11

Lead plate (Note 5)

Note 5: Lead directly over steel usually lacks good covering power, and unless a heavy deposit is to be used, cycles I-12 and I-13 are preferred.

Cycle I-12

Copper strike

Rinse

Acid dip (see Note 6): 2-10% Fluoboric acid, 2-10% acetic acid, or 2-10% hydrochloric acid

Rinse

Lead plate

Cycle I-13

Nickel flash

Rinse

Rinse

Lead plate

Note 6: The acid dip may be omitted, sometimes advantageously, if extra rinsing is used.

For chromium electroplating. Chromium directly on steel is usually for functional purposes and is known as hard chromium plate.

Cycle I-14

Proceed after the last rinse in cycle I-1, I-2, or I-3 as follows:

Anodic in chromic acid solution
Chromium plate
Cycle I-15
Stress relieve at 175 C (350F) if necessary
Anodic clean
Rinse
Anodic in chromic acid solution
Chromium plate
Rinse
Bake at 175 C (350F) to remove occluded hydrogen

PHOSPHATE COATING PROCESS

Phosphate coatings are specified by the metal finishing engineer for a variety of end uses and may be formed on the surfaces of iron, steel, galvanized steel, aluminum and electrodeposited zinc and cadmium. Phosphate coatings are used to promote the adhesion of organic coatings to metal substrates and to retard the rate of interfacial corrosion. Phosphate coatings are used to retain and enhance the performance of corrosion resistant oils and waxes on metallic surfaces. Phosphate coatings, with supplementary lubricant, are used to assist in cold deformation processes such as wire drawing, cold heading and impact forming. Phosphate coatings are able to provide these valuable functions because of their particular composition and structure. They are formed by the controlled corrosion of the metal surface being treated. The resulting coating is tightly bonded to the surface and is mineral in nature. The coating has a definite chemical composition and crystal structure. When fully developed, the coating will cover the surface completely and can be shown to exhibit electrical insulating properties.

The selection of the best coating for a particular application can be facilitated by an understanding of the characteristics of various coatings now being applied in commercial practice. Of particular importance is the physical structure. A series of scanning electron micrographs illustrates the difference in structure. A typical manganese phosphate coating on steel is characterized by a dense block-like deposit of angular crystals densely packed in a random orientation. This heavy coating provides a corrosion resistant or lubricating surface when the proper oil is applied in a supplementary treatment. The composite system of manganese phosphate and oil is used to reduce wear and prevent galling of moving parts such as piston rings, shafts, gears, cylinders, and pistons. In some cases, the etch pattern formed in the metal surface by the formation of the manganese phosphate coating is also of importance since it promotes oil retention on the sliding surface after break-in.

Heavy zinc phosphate coatings on steel exhibit a more platelike structure than manganese phosphate. Two varieties are normally encountered. When maximum corrosion protection is desired, an iron content is maintained in the phosphating solution and a crystal structure is produced. The orientation is principally parallel to the metal surface and the layered structure offers an excellent surface for the retention of corrosion resistant oils and waxes.

When a heavy zinc phosphate is used to facilitate cold deformation such as encountered in the drawing of wire and tubing, cold shaping, cold extrusion, etc., the phosphating solution is operated under iron-free conditions resulting in a crystal structure showing a high percentage of crystals oriented vertically to the metal surface. These thin plates may be lubricated by one of several methods, including lime, borax, specialized soaps and oils. In some cases, the surfaces of the individual crystals may be converted to a zinc soap. These lubricated plates then provide a multitude of slipping surfaces that promote the ease of cold deformation.

When a phosphate coating is used to promote paint bonding on steel or zinc-coated steel, a number of options are available to the finishing engineer. A zinc phosphate coating may be desired for superior

performance in retarding the lateral creep of corrosion between the organic coating and the metal originating at a scratch through the coating to the metal. Typical crystal structures for a zinc phosphate formed from the same solution on steel and galvanized steel. The coating on steel is tightly bonded to the surface and the effective surface area of the phosphate coating is considerably greater than the underlying metal. The phenomenon assists in increasing the adhesion of the organic coating which is further promoted by increasing the numbers of sites for mechanical locking of the coating to the phosphate crystals.

A zinc phosphate coating on a galvanized surface shows a different structure. In this case, the individual crystals are well defined and are distributed in a random orientation on the surface. Note that these photomicrographs are at a higher magnification than that used for the corrosion resistant or drawing phosphates. A fine-grained phosphate is desirable for a paint base in order to provide acceptable gloss with minimum organic coating thickness.

A less expensive but still effective phosphate treatment to promote paint bonding utilizes a so-called iron phosphate treatment on steel or zinc rich surfaces. It consists of an extremely fine-grained deposit of mixed oxides and phosphates of iron. The crystal structure is so fine that the coating is often classified as amorphous. When the same solution used to produce this coating on steel is used to treat a galvanized surface. This coating differs in structure and composition from that produced on steel and has the characteristics of a fine-grained zinc phosphate.

Another popular prepaint treatment is calcium modified zinc phosphate. The coating consists of densely packed granular crystals showing a high degree of uniformity that create a surface with greatly increased surface area and an intricate void pattern well-suited to provide a high degree of mechanical lock of the organic coating to the treated surface.

Amorphous Phosphate Coatings on Aluminum Surfaces

Coatings consisting mainly of aluminum and chromium (trivalent) phosphates with traces of other elements are formed on aluminum alloy surfaces by treating them with acid aqueous solutions containing phosphorus (pentavalent), chromium (hexavalent) and fluorine. Other elements may be present in the solutions including boron, silicon, zirconium, titanium, etc. These coatings are characterized by a degree of crystallinity too low to be readily detected by electron diffraction or X-ray techniques. They are accordingly designated as amorphous.

The chemistry of formation of these coatings is not entirely understood. Apparently direct oxidation of the aluminum surface by the hexavalent chromium and hydrogen ion couple in the presence of the phosphate radical leads to the formation of trivalent chromium and aluminum phosphate layer. The role of either the fluoride or complex fluoride seems to be one of depassivation. Suffice it to say that very little fluorine appears in the coatings produced.

While the coatings described may be considered to be typical of several of the types available, their structure and performance may vary with the specific chemical composition and operating conditions of the phosphating solution as well as a variety of other factors, including the composition of the metal being treated, its physical form and surface history; its degree of cleanliness and surface activation, the effectiveness of rinsing between stages, and the nature of any seal or other post-treatment that may be applied. The chemical compositions used to clean, activate, phosphate, seal or post-treat are usually proprietary products and the specific recommendations of the supplier should be followed. However certain general comments may be beneficial.

Because the metal surface being phosphated participates in the chemical reaction to form the coating, the ease and uniformity of its ability to corrode in the reaction plays an important part in proper coating formation. The chemical and physical nature of the extreme outer surface is much more important than the same properties for the article as a whole. The presence of stressed areas due to cold working, the

presence of previously applied corrosion resisting films, the possibility of decarburization, and the existence of pre-established etching patterns, all have an influence on the proper development of the phosphate coating.

In contrast to the stringent cleaning requirements for electroplating, the surface to be phosphated should be cleaned and conditioned by techniques designed to form a large number of active sites on the surface in order to form a fine-grained phosphate coating with even coverage. In general, minimal chemical cleaning is indicated. Mechanical methods for rust removal are preferred. Grit blasting and tumbling procedures are effective and are preferred over acid types of pretreatment. Organic contamination may be removed by solvent degreasing procedures, emulsion cleaning or alkaline cleaning, providing that the cleaner will not inhibit the surface and interfere with phosphate coating formation. In the case of iron phosphates used as a pre-paint treatment, the cleaning and phosphating operations may be performed by the same solution. When the maximum in grain refinement is required, a conditioning process is included. The active materials tend to be finely divided to colloidal in nature and their application increases the number of active sites for the development of the phosphate coating. Sometimes this procedure may be incorporated in the cleaning steps but, preferable, it is applied as separate treatment after cleaning. The effective life of these solutions is limited and they should be changed frequently for maximum effectiveness.

In the case of manganese and zinc phosphating solutions, the chemical composition is such that it provides a source of these elements in solution together with a source of phosphate. The function of these essential ingredients is often enhanced by the presence of oxidizing materials such as nitrate, nitrite, or chlorate. These materials accelerate the formation of the phosphate coating by increasing the aggressiveness of the acid solution. In addition, the solution may also contain catalytic amounts of other metals, complexing agents, and depolarizing agents.

Conventional chemical control of these solutions may include the determination of free acid, total acid and ferrous iron. The free acid is expressed as the number of milliliters of tenth normal sodium hydroxide, often referred to as "œpoints," necessary to titrate a known volume, usually ten milliliters of phosphate solution to a pH of 4.0. Total acid is the number of milliliters of tenth normal sodium hydroxide required to titrate the same volume of sample to a pH of 8.2. Ferrous iron is usually determined by titration with potassium permanganate.

The free acid maintains the solubility of the zinc or manganese phosphate and provides a measure of degree of aggressiveness of the phosphating solution toward the metal to be coated. Usually maximum-coating rates will be obtained when the free acid is only slightly higher than that necessary to maintain solubility of the metal phosphates in the working solution.

The total acid may be considered to be a measure of the amount of coating materials in solution and its ratio to the free acid is more significant than either individual value. The ratio of total to free acid in a liquid concentrate is usually lower than that of the operation bath and either partial neutralization or processing of scrap work may be necessary to establish the proper balance between the free and total acid. The latter procedure also establishes an iron level in the solution, which is generally desirable when the phosphate coating is applied to assist in corrosion protection. When the phosphate is to be used in a cold deformation process, soluble iron is excluded from the solution by the use of an oxidizing agent such as sodium nitrite. Whenever ferrous metals are phosphated, a stock loss is generated and iron is introduced into the phosphate solution. Ultimately this results in the formation of ferric phosphate, which has very limited solubility. This material is the principal ingredient in the sludge, which is generated as an inevitable by-product of the phosphating process. It may be removed by filtration or settling and decantation. Both high-temperature and low-temperature and phosphating solutions will produce sludge.

The production of another insoluble material, scale, is characteristic of phosphate solutions operated at high temperature. A general characteristic of zinc and manganese phosphating solutions is that the metal

phosphates become less soluble as the temperature is raised. This leads to selective deposition of scale on those surfaces that have the highest temperature; i.e., the heating surfaces used to maintain the operating temperature. When possible, the development of this type of scale may be limited by the use of a tank within a tank type of construction wherein the annular space between the tanks contains a suitable heat transfer fluid, or by the use of a properly designed external heat exchanger.

Phosphating solutions are sensitive to metallic contamination and materials such as lead and aluminum should be excluded in those cases where the solution is not designed to compensate for the introduction. Obviously, the introduction of cleaner residues and organic contamination will have a detrimental effect on the proper operation of a phosphating solution.

COBALT PLATING

Cobalt plating has white shine, good lustre and hard surface, but it is very costly metal, and its properties are very similar to those of nickel, owing to high cost factor it is very rarely used. So it is very less used in specialized areas due to its special magnetic properties.

Electrolyte composition and operational conditions for electroplating cobalt are described below:

Electrolyte composition for Bright Cobalt Palating

Constituents	Qty.
Cobalt Sulphate	300 gms/litre
Cobalt Chloride	50 gms/litre
Boric Chloride	30-40 gms/litre

The working conditions of cobalt electrolyte corresponds in the main with those used for nickel deposition, greater current density can be used and the operational temperature is kept at 50°C and pH value should be 4.

Another solution for cobalt plating is given below:

Alter Cobalt Plating Bath Composition

Constituents	Qty.
Cobalt Sulphate	450 gms/liter
Boric Acid	28 gms/liter
Sodium Chloride	10 gms/liter
Water	1 liter

Bath temperature is maintained at 35°C and current density is 150 amps./sq.ft.

Here is should be noted that corrosion behaviour of cobalt deposits is generally regarded as good. Without chromium plating it is almost better than nickel, due to its colour and adequate corrosion protection properties. So it has achieved some importance in the last few years in unchromed state, for example spectacle frames. In the chromed condition its behaviour is similar to that of nickel.

GOLD ELECTROPLATING

INTRODUCTION

Gold (Au= 197.2 atomic weight) is generally found in the metallic state. It is one of the metals possessing a yellow colour. Precipitated from its solution with green vitriol (ferrous Sulphate) or oxalic acid, it appears as a brown powder without luster, which on pressing with the burnisher acquires the colour and luster of gused god. Pure gold is nearly as soft as lead, but posses considerable tenacity. In order to increase the hardness when used for articles of jewellery and for coinage, it is alloyed with silver or copper. The "Fineness of Gold" or its proportion in the alloy is usually expressed by stating the number of carats present in 24 carats of the mixture. Pure gold is stated to be 24 carats "fine" standard gold is 22 carats fine, 18

carat gold is a mixture of 18 parts of gold and 6 of alloy. Gold is the most malleable and ductile of the metals. It may be beaten out into leaves not exceeding 1/10,000 of a millimeter in thickness.

When beaten out into thin levels and viewed by transmitted light, gold appears green, when very finely divided it is dark red or black. The specific gravity of fused gold is 19.35 and that of precipitated gold powder, from 19.8 to 20.2. Pure gold melts at about 2016°F and in fusing exhibits a sea green colour, 23 carat gold melts at 2012°F, 22 carat at 2009°F, 20 carat at 2002°F, 18 carat at 1995°F, 15 carat at 1992°F, 13 carat at 1990°F, 12 carat 1987°F, 10 carat at 1982°F, 9 carat at 1979°F, 8 carat at 1973°F, carat at 1960°F.

Gold salts contain 40 percent fine gold and have to be dissolved in water. Anodes of pure gold are preferable, although platinum or carbon anodes may be used. If gold anodes are not used, the gold is necessarily taken from the solution more rapidly.

Brass or copper articles to be gold plated are immersed in the gilding solution with the gold anode held in the right hand (used to agitate the gilding solution slightly), the articles held in the left hand being wired as negative or cathode. About half minute is suffice to obtain a good deposit; if a thicker deposit is required the articles are swilled and scratch brushed, and then given a further 10 second in the gilding bath to get a bright finish. Articles made of base metals, or soft soldered, are first plated in a cyanide copper solution. Articles, which require bright gilding inside, are first burnished, given a cleaning bath and then put through the potassium cyanide solution. Large articles are filled with gold solution and connected to the cathode rod, a piece of gold wrapped in two or three pieces of swan's down is connected by a wire to the anode is suspended in the solution inside the article and moved about briskly for a time, depending upon the thickness of deposit required. If the edges are to be gilded, the anode is rubbed on these parts. A fasted appearance is obtained by sand blasting or using a brushing wheel, then gilding and scratch brushing again.

Stripping Gold

The electrolytic process is used for stripped gold from plated articles. The solution is made up of 500 gms. Potassium cyanide, 250 gms. Caustic soda and one-gallon water. The articles are used as anodes and are hung on the center rod. Sheet steel cathodes are suspended from the outer rods, which are connected to the negative pole of the dynamo a resistance board being used to regulate the current.

Gold Baths

Gold plating may be effected in a hot or cold bath, large objects being generally plated in the latter and smaller objects in the former. The hot bath has the advantage of requiring less current-strength, besides yielding deposits of greater density and uniformity and of sadder richer tones. Hot baths work with a moderate content of gold " 11.5 to 12.5 grains per quaint of bath-while cold baths should contain not less than 54 grains per quaint.

Baths prepared with potassium Ferro cyanide are preferred by some authors, while others work with a solution of gold salt and potassium bicarbonate and others recommend a solution of cyanide of gold in potassium cyanide. With proper treatment of the bath good results may be obtained with either. Generally, the use of baths prepared with potassium ferrocyanide can not be recommended on account of the secondary decompositions which take place during the operation of plating and because the baths do not dissolve the gold anodes. Below only approved formulas for the preparation of gold baths will be given.

Bathfor Cold Gilding

Fine gold in the form of fulminating gold 54 grains, 98% potassium cyanide 0.35 to 0.5 oz (according to the current strength used), water 1 quiant.

Electro-motive force at 10 cm electrode distance and with the use of 0.35 oz. Of potassium cyanide, 1.35 volts, with the use of 0.5 oz of potassium cyanide, 1.2 volts.

Current-Density, 0.15 Ampere

To prepare this bath, dissolve 54 grains of fine gold in aqua regia in a porcelain dish heated over a gas or alcohol flame and evaporate the solution to dryness. Continue the heating until the solution is thickly fluid and dark brown and on cooling congeals to a dark brown mass. Heating too strongly should be avoided, as this would cause decomposition the auric chloride would be converted into aurous chloride and eventually into metallic gold and chlorine, which escapes. The neutral chloride of gold formed in this manner is dissolved in 1 pint of water and ammonia added to the solution so long as a yellow-brown precipitate is formed, avoiding, however a considerable excess of ammonia. The precipitates of fulminating gold is filtered off, washed and dissolved in 1 quart of water containing 0.5 oz of potassium cyanide in solution. The solution is boiled, replacing the water lost by evaporation, until the odor of ammonia which is liberated by dissolving the fulminating gold in potassium cyanide disappears, when it is filtered. Instead of dissolving the gold and preparing neutral chloride of gold by evaporating, it is more convenient to use 108 grains of chemically pure neutral chloride of gold as furnished by chemical works and precipitate the fulminating gold from its solution.

Too large and excess of potassium cyanide yields good deposits of an ugly, pale colour when working with a more powerful current the excess of potassium cyanide need only be slight, with a weaker current it may be larger.

The fulminating gold must not be dried as in this condition it is highly explosive but should be immediately dissolved while in a moist state.

If the cost of bath for cold gilding with such as high content of gold as given in formula 1 should appear too great, only 27 grains of gold per quart may be used. Within a suitable electro motive force deposits of a beautiful shade-yellow colour are thus also obtained. Such a bath is yielded by the following formula:

Dissolve the gold salt from 0.35 oz. Of fine gold or about 0.7 oz of neutral chloride of gold in \hat{A} $\frac{1}{2}$ pint of the water and the potassium cyanide in the other \hat{A} $\frac{1}{2}$ pint of water and after mixing the solutions boil for half an hour. The preparation of this bath is more simple than that of formula I, but the colour of the gold deposit obtained with the latter is warmer and sadder. The high content of gold in the bath, prepared according to formula. (II) Readily cause a red-brown gold deposit and hence special attention has to be paid to be the regulation of the current.

Formula for Cold Gold Gilding Bath

Formulation for Cold Gold Gilding Bath

Ingredients	Quantity
(II). Fine gold as neutral chloride of gold	0.35 oz
98% potassium cyanide	0.7 oz
Water	1 quart
Electro motive force at 10 cm electrode distance	About 1.5 volts,
Current density	0.12 ampere

Formulation for Cold Gold Gliding Bath

Ingredients	Quantity
(III) Yellow prostate of potash (potassium ferrocyanide)	0.5 oz.
Carbonate of Soda	0.5 oz
Fine gold (as chloride of gold or fulminating gold)	30.75 grains

Water	1 quart
Electromotive force at 10 cm electrode distance	2 volts
Current density	0.15 ampere

For those who prefer gold baths prepared with yellow prostate of potash instead of potassium cyanide the following formula for cold gilding is given.

To prepare the bath heat the solutions of the yellow prostate of potash and of the carbonate of soda in the water to the boiling-point, add the gold-salt and boil $\frac{1}{4}$ hour, or with use of freshly precipitated fulminating gold, until the odor of ammonia disappears. After cooling, the solution is mixed with a quantity of distilled water, corresponding to the water lost by evaporation and filtered. The bath gives beautiful bright gilding upon all metals, even upon iron and steel.

The yellow prostate of potash baths are deservedly popular for decorative gilding, when gold deposits of different colours are to be produced upon an object. Certain portions have then to be covered with stopping off varnish, the latter being less attacked by this bath than by one containing an excess of potassium cyanide.

This bath is especially suitable for the so-called clock gilding. The articles are first provided with a heavy deposit of copper in the alkaline copper bath next drawn through the bright-pickling bath, thoroughly rinsed, and finally gilded in the bath heated to about 122°F .

Gold Baths for Hot Gilding

Formulation for Hot Gold Gilding Bath

Ingredients	Quantity
Fine gold (as fulminating gold)	15.4 grains
98% potassium cyanide	77 grains
Water	1 quart
Electro-motive force at 10 cm electrode distance	1.0 volts
Current-density	0.1 ampere

This bath is prepared in the same manner as that according to formula I, from 15.4 grains of fine gold, which is converted into neutral chloride of gold by dissolving in aqua regia and evaporating or dissolve directly 29.32 to 30.75 grains of chemically pure neutral chloride of gold in water, precipitate the gold as fulminating gold with aqua ammonia, wash the precipitate, dissolve in water containing the potassium cyanide and heat until the odor of ammonia disappears, replacing the water lost by evaporation. This bath yields a beautiful shade gilding of great warmth. All that has been said in regard to the content of potassium cyanide in the bath prepared according to formula I also applies to this bath. The temperature should be between 158° and 176°F and the current strength 2.0 to 2.5 volts following bath is recommended for hot gilding.

If this bath is to serve for directly plating steel, only half the quantity of potassium cyanide is to be used and the objects should be covered with the use of a some what greater electro-motive force. Increasing the content of neutral sodium to 0.5 or 0.7 oz also appears advisable.

Dissolve in a porcelain dish, with the aid of moderate heat, the sodium phosphate and sodium Sulphate and when the solution is cold add the neutral chloride of gold prepared from 15.43 grains of gold is equal to about 30.86 grins of commercial chloride of gold, and the potassium cyanide. For use, heat the bath to between 158°F and 167°F and 167°F .

Formulation for Hot Gold Gilding Bath

Ingredients	Quantity
Chemically pure catalyzed sodium phosphate	2.11 oz
Neutral Sodium Sulphate	0.35 oz
Potassium Cyanide	30.86 grains
Fine Gold (as chloride)	15.43 grains
Distilled Water	1 quat
Electromotive force at 10cm electrode distance	1.5 volts
Current density	0.12 ampere

For the preparation of gold baths for hot and cold gilding, double gold salts and triple gold salts as well as gold solutions, as brought into commerce by some manufacturers may also be used.

Many gold-platters prepare their gold baths with the assistance of the electric current. This is accomplished as follows:

Dissolve 12 ozs of potassium or sodium cyanide (98 to 99%) in a gallon of distilled water and heat a temperature of 130°F. Place in this cyanide solution a porous cup which is attached to the negative or cathode rod. A carbon cathode is suspended in the porous cut, which must contain sufficient cyanide solution to bring it to the same level or a little higher, than the outside solution. Place an anode of fine gold weighing about 1.5 oz. Troy in the larger solution of cyanide, attaching it to the positive rod. Allow an electric current from two Bunsen cells or a dynamo to pass at an electromotive force of from 3 to 4 volts until 1 odwts of gold have been dissolved. The solution after removing the porous cup is ready for use.

The only advantage of this mode of preparing the bath is that it excludes a possible loss of gold, which may occur in dissolving god, evaporating the gold solution, etc. by breaking the vessel containing the solution. However, by using commercial chemically pure chloride of gold such loss is avoided and the bath prepared according to the formulae given yields richer tones than a gold bath produced by electrolysis. Besides, the preparation of the gold bath with the assistance of the electric current can only be considered for smaller baths, since the saturation of a larger volume of potassium cyanide solution requires considerable time and the potassium cyanide is strongly decomposed by long heating.

Tanks for Gold Baths

Gold baths for cold gilding are kept in tanks of stoneware or enameled iron, or small baths in glass tanks, which to protect them against breaking are placed in a wooden box. Baths for hot gilding require enameled iron tanks in which they can be heated by a direct fire, or better, by placing in hot water (water bath) or by steam. For small gold baths for hot gliding porcelain dish resting upon a short-legged iron tripod may be used. Beneath the iron tripod is a gas burner supplied with gas by means of a flexible India-rubber tube connected to an ordinary gas burner. Across the porcelain dish are placed two glass rods, around which the poles wines are wrapped. In heating larger baths in enameled tanks over a direct fire it may happen that on the places most exposed to the heat the enamel may blister and peel off it is, however better to heat the baths in a water or steam bath. For this purpose have made a box of stout iron or zinc sheet about ¾ inch wider and longer, and about 4 inches deeper than the enameled tank containing the gold bath.

Execution of Gold-Plating

Most suitable current density, 0.15 to 0.2 ampere. Like all other elector-plating operations, it is advisable to effect gold plating with an external source of current, this is to use a battery or other source of current separated from the bath.

The apparatus required for salt water gold solution is as follows. A copper kettle having a steam coil of copper pipe at the bottom, a red porous jar and a piece of sheet zinc ½ inch thick, which should be formed

into the shape of a cylinder. To the latter is riveted a copper rod, so shaped that it extends over and above the opposite side of the zinc cylinder. Place the porous jar and zinc on glass insulators in the bottom of the copper kettle. In the water surrounding the porous jar dissolve rock salt until the brume hydrometer registers 15 degrees. The gold solution which should be made with yellow prostate of potash is placed inside the porous jar. The copper kettle, zinc and rock salt generate a feeble current of electricity, which deposits the gold upon articles suspended from the copper rod and immersed in the gold solution, the temperature of which should be maintained at 170°F .

The gold deposit seldom needs to be made extravagantly heavy and the rough surface formed would require more laborious polishing with the burnishers and on the other, the gold deposits adhere quite well to highly polished surfaces, provided the current-strength is correctly regulated and the bath accurately composed according to one of the formulae given.

The current-strength must, under no circumstances be so great that a decomposition of water and consequent evolution of hydrogen on the objects, take place, since other wise the gold would not deposit in a and coherent form, but as a brown powder. By regulating the current-strength so that it just suffices for the decomposition of the bath and avoiding a considerable surplus a very dense and uniform deposit is formed and by allowing the object to remain long enough in the bath, a beautiful, mat gold deposit can be obtained in all the baths prepared according to the formulae given. It may, however, be mentioned that this mode of mat gilding is the most expensive, since it requires a very heavy deposit, and it will therefore, be better to matten the surface previous to gilding.

For gilding with cold baths, two freshly-filled Bursen cells coupled for electro-motive force suffice in almost all cases, while for hot baths one cell is as a rule, sufficient, if the anode surface is not too small. The more electropositive the metal to be gilded is, the weakens the current can and must be.

Though gold solutions are good conductors and therefore, the portions of the articles which do not hang directly opposite the anodes gild well, for solid plating of larger objects it is recommended to frequently change their positions, except when they are entirely surrounded by anodes.

The inner surfaces of hollow-ware, such as drinking-cups, milk pitchers, etc. are best plated after freeing them from grease and pickling, by filling the vessel with the gold bath and suspending a current-carrying gold anode in the center of vessel, while the outer surface of the latter is brought in contact with the negative conducting wire the lips of vessels are plated by placing upon them a cloth rag saturated with the gold bath and covering the rag with gold anode.

For Gold-Plating in the Cold Bath the Process is as Follows

The objects, thoroughly freed from grease and picked (and if of iron, zinc, tin, Britannia, etc. Previously coppered) are suspended in the bath by copper wires, where they remain with a weak current until in about 8 or 10 minutes they appear uniformly plated. At this stage they are taken from the bath, rinsed in a pot filled with water and the latter, after having been used for some time, is added to the bath to replace the water lost by evaporation. The articles are finally brushed with a fine brass scratch-brush and tartar solution, thoroughly rinsed, again freed from grease by brushing with lime paste and then returned to the bath, where they remain until they have acquired a deposit of sufficient thickness.

When an article is to have a very heavy deposit, it is advisable to scratch-brush it several times with the use of tartar or its solution, or with a solution of size and water between the intermediate coats of gold. By these means a very durable and lasting coating of gold will be secured.

For gold plating with the hot bath, the operations are the same, with the exception that a weaker current is introduced into the bath and the time of the plating process shortened frequent scratch brushing also increases the solidity of the deposit and prevents its prematurely turning to a dead brown-black. Since in hot plating more gold than intended is readily deposited it is especially advisable to place a rheostat and

voltmeter in the circuit, as otherwise the operator must remain standing along side of the bath and regulate the effect of the current by immersing the anodes more or less.

When taken from the bath, the finished gilded objects should show a deep yellow tone, which after polishing yields a full gold colour. If the objects come from the bath with a pale gold tone, the deposit, after polishing shows a meager, pale gold colour, which is without effect. Gold deposits of a dark or brown colour also do not yield a shade gold tone.

With a somewhat considerable excess of potassium cyanide and if the objects to be plated are not rapidly brought in contact with the current-carrying object rod, hot gold baths cause the solution of some metal. Therefore when silver or silver plated objects are constantly plated in them they yield somewhat greenish gilding in consequence of the absorption of copper, if copper or coppered articles are constantly plated in them. Hence, for the production of such green or reddish colour, gold-plating baths, which have thus become argentiferous or cuprififerous, may be advantageously used.

CORROSION AND THEIR PREVENTIVE MEASURES AND POLLUTION CONTROL CONSIDERATION

Introduction

As is known, metals have shaped the development of modern world. This is why metals are:

- (1). World's increasing wealth,
- (2). Aspiration of the nation and
- (3). Demand of our civilization. But metal do deteriorate because of their reaction with environment, namely
 - (1). Industrial atmosphere, (2) marine atmosphere,
 - (3) Rural atmosphere, and (4) aqueous solutions (pH 0-14), etc. This results in huge metal loss incurring 1.5% of GNP.

Corrosion has been defined in many ways. A sub-committee of the Inter Society Corrosion Committee recommends the definition:

“Corrosion is the deterioration of a substance (usually a metal) because of a reaction with its environment. The corrosion is stated to be an electrochemical phenomenon”.

Corrosion Costs

U.K.	1300 million/year
Australia	A\$ 2000 million/year, 1.5%GNP
India	Rs.8000 crores/year

Corrosion Loss in System

Automobile	100 milion/year
Auto radiators	\$52 million/year
Auto exhaust	\$500 million/year
House water heaters	\$3 million/year

Corrosion leads to Numerous Damages, which are as below:

- Appearance
- Plant shut down
- Contamination of products
- Loss of valuable products
- Effects of safety and reliability
- Maintenance and operating costs
- Loss of life
- Badly rusted items leave impression. Here, service life versus dollars is not the controlling factors.

- Frequent shut down are due to lack of knowledge, neglect and ignorance about corrosion.
- Market value of the products, pigments, foods, drugs, semi-conductor is related to its purity and quality. This demands expensive material of construction.
- Economizing on materials of construction is not desirable, if safety is risked.
- Substantial savings if close co-operation between the corrosion engineers and process and design personnel.

In fact, our economy would be drastically changed if there is no "corrosion". While corrosion is inevitable, its cost can be reduced considerably by judicious selection of preventive measures.

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